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# Isothermal δ/α' Transformation and TTT Diagram in a Plutonium Gallium Alloy

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## ABSTRACT

Differential scanning calorimetry (DSC) is used as an alternative approach to determining the tine-temperature-transformation (TTT) diagram for the martensitic delta to alpha-prime transformation in a Pu-2.0 at% Ga alloy. Previous work sugests that the TTT diagram for a similar alloy exhibits an unusual double-C curve for isothermal holds of less than 100 minutes. Here, we extend this diagram to 18 hours, and confirm the double-C curve behavior. When the sample is cooled prior to the isothermal holds, the delta to alpha-prime transformation is observed as several overlapping exothermic peaks. These peaks are very reproducible, and they are believed to be the result of different kinds of delta to alpha-prime martensitic transformation. This may be due to the presence of different nucleation sites and/or different morphologies.

## INTRODUCTION

Under ambient conditions, the thermodynamically stable phase of pure plutonium is the brittle monoclinic alpha phase. However, alloying plutonium with a few atomic percent of an element such as gallium causes the malleable face-centered-cubic delta-phase to be retained at ambient temperatures [1]. For Pu-Ga systems at ambient conditions, the delta-phase is metastable and gives rise to an extremely slow eutectoid decomposition to alpha + $Pu_3Ga$ [2]. When the delta phase is cooled to sub-ambient temperatures, a partial transformation to the metastable alpha-prime martensitic phase occurs. This alpha-prime phase is similar to the alpha-phase, but it has Ga trapped in the lattice. Previously, the delta to alpha-prime phase transformation (at about -120ºC) and its reversion (at about +30ºC) in a Pu-2.0 at% Ga alloy have been studied using continuous cooling and heating cycles in a differential scanning calorimeter, a resistometer and a dilatometer [3, 4, 5]. Although the delta to alpha-prime transformation can be observed with continuous cooling experiments, it is reported to be an isothermal martensitic transformation [2, 5, 6].

Here, we investigate the delta to alpha-prime isothermal martensitic transformation behavior as a function of time and temperature. In fact, this delta to alpha-prime transformation is reported to have unusual double-C curve kinetics in a Time-Temperature-Transformation (TTT) diagram [5]. This TTT diagram for a 1.9 at.% gallium alloy was obtained using dilatometry in the temperature range +60ºC to -155ºC, and it is reproduced in Figure 1. In their report, Orme, et al. believed the transformation to be martensitic and possibly massive at higher temperatures, with nucleation being time-dependent and thermally-activated. Growth of the martensite particles in the Pu-1.9 at% Ga alloy was relatively slow compared to other Pu-Ga alloys (on the order of minutes, compared to seconds for alloys with lower Ga contents) [5].

Because the TTT diagram published by Orme, et al. [5] contains only 19 data points and because the double-C behavior has not been confirmed by other researchers, our goal is to thoroughly investigate the isothermal behavior of the delta to alpha-prime transformation.

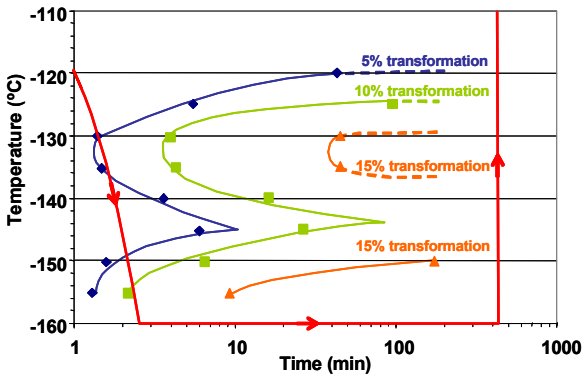


**Figure 1.** Time-Temperature-Transformation diagram for a Pu-1.9 at.%Ga alloy [5]. This TTT diagram shows the unusual double-C curve kinetics for the delta to alpha-prime transformation. Here, we have extended this TTT diagram to 18 hours. The dark line with arrows shows the thermal profile of an experiment with an 18 hour isothermal hold at -160ºC.

Furthermore, Orme, et al.'s diagrams only extend to several hundred minutes, and in the current work we examine the transformation over the course of 18 hours. Here, we use an alternative approach to determining TTT diagrams using differential scanning calorimetry (DSC). Preliminary results from this approach suggest a confirmation of the double-C behavior in a Pu-2.0at%Ga alloy.

## EXPERIMENTAL DETAILS

A single Pu-2.0 at% Ga alloy sample was used in all experiments. The impurity content without gallium was 1600 weight ppm, including 1000 ppm of delta-phase stabilizing elements (Al, Am, Ce, etc.) and 400 ppm of alpha-phase stabilizing elements (Np, U, etc.).The sample was a 2.8 mm diameter cylinder with a length of 3mm and a mass of 250 mg. The sample had with two opposing flats running parallel to the cylinder axis to provide good thermal contact with the sample pan.

One initial heat treatment was performed at 430ºC for 12 hours to produce a partial uniform gallium distribution throughout the grain and to assure that the sample was all in the delta phase [7]. Following this anneal, the sample was cut to size with a diamond saw. The cutting speed was < 30.5 m/min, the depth of cut per revolution was about 0.05 mm, and trichloroethylene was use as the cutting fluid. The surface oxide was removed by mechanical polishing and electropolishing. The specimen was placed in a holder in the electropolishing cell and allowed to cool in the solution for about 30 seconds. The electropolishing solution composition, by volume, was 10% nitric acid (70% concentration), 45% methanol and 45% butoxyethanol (to decrease the flash point). The parameters for electropolishing were as follows: -20ºC, 115V at about 50 mA for 2-3 seconds (the electropolishing speed was about 2µm/sec). Finally, the sample was annealed at 175ºC for 30 minutes to revert any mechanical alpha-prime that may have formed on the surface during polishing.

The sample was encapsulated in a gold-lined stainless steel pan, which sealed with a gold-plated copper gasket. These pans are designed for high pressure DSC studies and can withstand 150 atm of pressure at 400ºC. Thus, they are ideal for safely containing radioactive materials in the DSC.

A Perkin-Elmer Diamond power-compensation DSC with liquid nitrogen cooling was used to measure the heat flow and transformation temperatures during thermal cycles and isothermal holds. The instrument was calibrated with adamantine (solid-solid transformation at 65.53ºC, $\Delta H$ = 24.78 J/g), indium (solid to liquid transformation at 156.6ºC, $\Delta H$ = 28.45 J/g) and zinc (solid to liquid transformation at 419.47ºC, $\Delta H$ = 108.37 J/g). The purge gas was a mix of 90%Ne/10%He, which can be used between -175ºC and 585ºC [8]. The cooling and heating rates were 20ºC/min. This rate was chosen because it is the fastest rate at which the DSC can reliably heat and cool the sample through the entire experimental temperature range. A fast cooling rate was selected to limit the amount of delta to alpha prime transformation during the cooling that precedes the isothermal hold.

Prior to each experimental run, the sample was annealed at 375ºC for 8 hours and then conditioned at 25ºC for 12 hours. Previous work [3, 9] demonstrates that conditioning treatments of at least 6 hours at 25ºC provide the needed time and temperature conditions for optimal alpha-prime formation.

For each experimental run, the sample was cooled from 25ºC to the isothermal hold temperature at 20ºC/min. The sample was held at a subambient temperature for 18 hours. Then it was heated to 350ºC and cooled back to 25ºC at 20ºC/min. The sample was repeatedly scanned and was not removed from the DSC after each cycle, so a baseline scan with empty pans could not be performed after each scan, as is conventionally done in DSC experiments. As an alternative, a curve obtained by a third order polynomial fit of the cooling curve in the temperature range of approximately 150ºC to -40ºC was subtracted from the raw data as the baseline. Then, a straight line was subtracted to correct the slope. This procedure facilitated comparisons of the runs. Although this method does not achieve absolute accuracy in the estimation of the heats of transformation or heat capacities, it provides a consistent method for comparing all of the transformation and reversion peaks.

## RESULTS AND DISCUSSION

Here, we investigated the amount of alpha-prime formed during long isothermal holds (18 hours) at specific sub-ambient temperatures between -90ºC and -160ºC. This is the temperature range encompassed by the existing TTT diagram for a similar alloy (1.9 at.% Ga) [5]. Orme, et al.'s work does not explicitly define time zero, but the TTT diagram indicates that transformation does not occur above -120°C. Therefore, for the present experiments, we define time zero as the time when the sample temperature reaches -120°C. For the isothermal holds at temperatures above -120°C, time zero occurs when the sample reaches the anneal temperature.

Prior to the isothermal hold, the sample was cooled to the hold temperature at 20°C/min. The DSC thermograms corresponding to this cooling are plotted in Figure 2. In this figure, it is clear that some delta to alpha-prime transformation did occur prior to each isothermal hold, except before the hold at -90°C. This transformation is observed as several overlapping exothermic peaks beginning at -100°C. These peaks are very reproducible and are believed to be the result of different kinds of delta to alpha-prime martensitic transformation. This may be due to the presence of different nucleation sites and/or different morphologies.

The heating portions of the thermal cycles corresponding to this reversion are shown in Figure 3. The reversion begins at +25ºC, which is in good agreement with the previously published value [6]. The study of the reversion curves did not show any intermediate phase

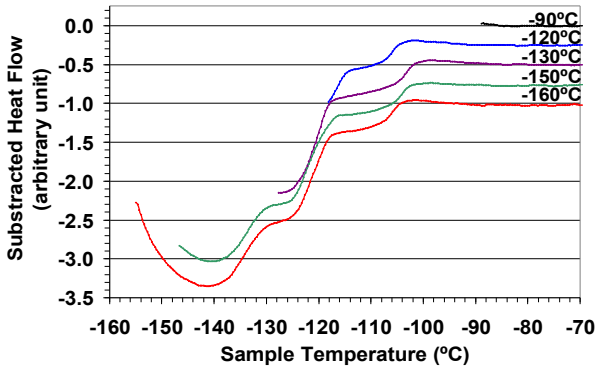


**Figure 2.** DSC thermograms corresponding to the $\delta \rightarrow \alpha'$ transformation during continuous cooling at 20ºC/min before each 18 hour anneal. This transformation is exothermic and begins at approximately -100ºC. The DSC data indicates that the transformation results in 3 overlapping exothermic peaks. The data have been offset along the y-axis for clarity.

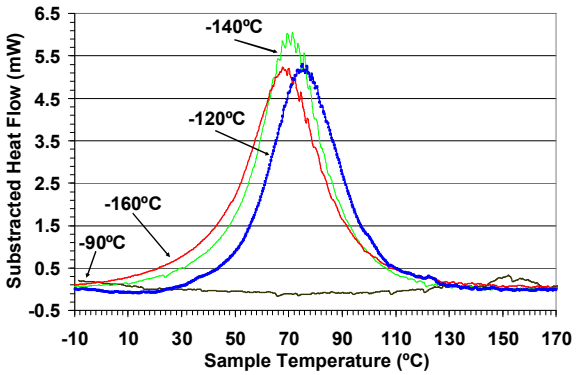


**Figure 3.** DSC thermograms corresponding to the $\alpha' \rightarrow \delta$ reversion upon continuous heating at 20ºC/min following each 18 hour isothermal hold. The temperatures on the plot correspond to the isothermal holding temperatures. This transformation is endothermic and begins at approximately 20ºC.

transformations such as those observed previously in low-gallium Pu alloys ($\alpha' \rightarrow \beta\ (\beta') \rightarrow \gamma\ (\gamma') \rightarrow \delta$) [10]. As the isothermal hold temperature is decreased, the peak temperature also decreases (Figure 4). This suggests that the different types of alpha-prime formed during the three overlapping peaks observed during cooling may also have slightly different reversion characteristics. An investigation of this observation will be the subject of future work

It was assumed that all alpha-prime formed during the holds reverted back to the delta phase during heating, and thus, the relative amount of alpha-prime formed during the cooling and isothermal holds was quantified by integrating the alpha-prime to delta (reversion) peak. We use this reversion peak because the isothermal alpha-prime formation during the isothermal holds is not distinguishable on the DSC thermograms. To compare the reversion peaks following each isothermal hold, the peaks were integrated over an interval of ±40 degrees on each side of the peak temperature. The peak temperature is the temperature where the rate of transformation is at a maximum (*i.e.*, the temperature where the heat flow is at a maximum value). The integrated area between the reversion peak and the baseline gives the heat of transformation ($\Delta H_{\alpha' \rightarrow \delta}$), which is proportional to the amount of alpha-prime formed. Some repeated runs with 18 hour

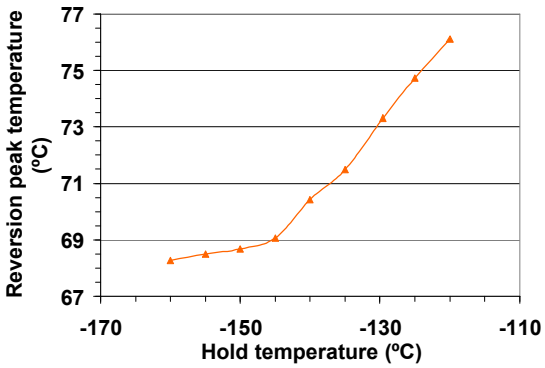


**Figure 4.** The α' → δ reversion peak temperature as a function of the isothermal hold temperature. The peak temperature shifts toward lower temperatures as the hold temperature decreases.

isothermal holds at -160ºC give an approximation of the error in the peak integration, which is less than ±50 mJ / total peak area. The error in temperature was twice the standard deviation of the sample temperature during 18h for each run, and it was less than ±0.05ºC.

The results of this 18 hour holds are shown in Figure 5. This plot is a cross-section of the TTT diagram at 18 hours. Instead of plotting a contour line of constant amount of transformation, as is traditionally done in TTT diagrams, the contour in Figure 5 is for constant time. This data suggests a confirmation of the double-C behavior because there are two temperatures at which local maxima in the amount of transformation occur (-130°C and -155°C). I inserted a nonbreaking hyphen to keep the negative sign on the same line as the number Between these two temperatures, there is a valley at -145°C where isothermal holds result in smaller amounts of transformation. Thus, these results suggest that the double-C behavior of the delta to alpha-prime transformation occurring over several minutes in a Pu-1.9at%. Ga alloy observed by Orme, et al. [5] is also observed when the isothermal hold extends to 18 hours.

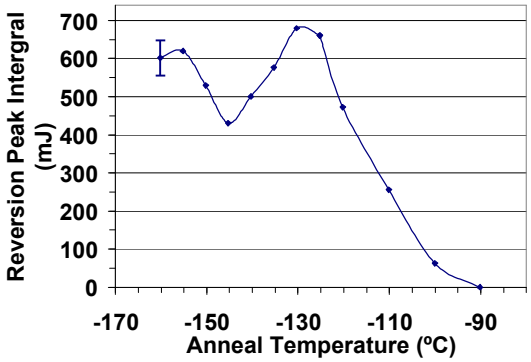


**Figure 5.** Integrated peak areas of the α' → δ reversion peaks following 18 hour isothermal holds versus anneal temperature. The amount of alpha-prime formed is related to the integral of the alpha-prime to delta reversion peak.

## CONCLUSIONS

The isothermal martensitic delta to alpha-prime transformation in a Pu-2.0 at% Ga alloy has been investigated. Previously, this transformation was reported to have double-C curve kinetics in a TTT diagram that extended to approximately 200 minutes. Here, differential scanning calorimetry was used as an alternative approach to investigate this behavior. A Pu-2.0 at% Ga alloy was held isothermally for 18 hours at various sub-ambient temperatures in the DSC, and the amount of alpha-prime formed during the hold was determined by integrating the area of the alpha-prime to delta reversion peak on heating. The data indicate two temperatures where local maxima in the amount of transformation occur during isothermal holding, -130°C and -155°C. At -145°C, less transformation occurs. Thus, a slice through the TTT diagram at a constant time (18 hours) suggests a confirmation of the double-C curve kinetics for the Pu-2.0 at% Ga alloy.

## ACKNOWLEDGMENTS

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